

GENERAL BIBLIOGRAPHY

1. The decomposition of carnallite, R. Block Vere Kertes and D. Dowy. Bull Research Council Israel 2, NO2 115-17 (1952) CA 47 2077e. Carnallite dissolved in brine solutions decomposition with precipitate of KCl. Convection currents are set up from the denser solution surrounding the carnallite to the less dense solution about the KCl. The KCl does not crystallize in contact with the carnallite.
2. Use of dyes in the solar evaporation of Dead Sea brine, Block, et.al. Ind. Eng. Chem. 43 1544 (1951).

Discussion of the use of organic dyes in increasing the evaporation rate of brine. Effect of pond depth, dye concentration, etc. are investigated.
3. The Dead Sea - A Storehouse of Chemicals Novomeysky, M.A. Trans Instn. Chem. Engrs, London 14 (1936) 60.

A comprehensive review of the early technology of potash production from the Dead Sea.
4. The use of brine in vacuum refrigeration and evaporation. D. Wittenberg Ind. Chemist 28 535-7 (1952). Power device proposed from Dead Sea brine CA 47 4009i.
5. Serowy, Fritz and Tittel, Manfred: Zur Frage der thermischen Behandlung von Carnallit und Bischofit (Mg C12.6H20) Berlin: Akademie-Verlag (1959) 88 pp DM 7. (book) also see Freiburger Forschungsh. CA 54 8000h A 128 58 ref.
6. Special problems in mineral salt research and utilization Fritz Serowy (Akad. Wiss., Arbeitsstelle Mineralsalzforschung, Berlin-Aldershof). Freiburger Forschungsh. A 123 287-302 (1959) CA 54 3875h. A discussion of suggested procedures in the refining of potash salts with a view to full utilization of the residual solutions.
7. Ion-exchange effects in concentrated salt solutions. Emmo Schmidt. Ibid 303-16. Use of this technique is not promising.

8. The sediment problem in the south Harz Potash Works. Fritz Dedekind (VVB "Kali", Erfurt, Ger.) Ibid 364-75. Technical problems in clarifying KCl solutions discussed.
9. Recovery of KCl from brines, Wm. B. Dancy and Albert Adams (to Int. Min. and Chem) U.S. 2,804, 371 August 27, 1957, Gypsum and CaCl_2 added to precipitate syngenite. Filtrate treated to fractionally crystallize KCl. CA 672h.
10. Continuous leaching of potassium minerals. Societe d'Etudes Chimiques pour l'Industrie et l'Agriculture (Jean Martin inventor) Ger. 956,303, January 17, 1957. CA 53 4676 g.

KCl is leached from minerals especially sylvanite, by continuous extn. with a stream of warm mother liquor, which holds the mineral suspension in a turbulent state.

11. Mixed salts from carnallite and impure sylvite. Otto Krull, Ger. (East) 10,814 November 26, 1956. CA 52 20955b.

By addition of artificial carnallite (I) the final solution is saturated with I, thus the loss of KCl is diminished. The amount of I is calculated on the basis of the MgCl_2 content or the d. of the hot concentrated solution.

12. The working up of crude mixed salt, O. Krull Bergbautech, 6 39-42 (1956) Method of separating crude carnallite and sylvite is given. CA 50 12412h.

13. The working up of mixed crude salt, O. Krull Bergbautech 6 39-42 (1956).

Crude carnallite and hard salt (crude sylvite) sometimes occur in an intimate mixture. Complete separation of the two is difficult. The best procedure is to grind the mixed salt to a size suitable for carnallite extn. Extract the carnallite, grind the residue, and wash it with a hard salt solution and water. Several different procedures can be used to extract the carnallite. One is extn. with a hot MgCl_2 -KCl solution which is poor in KCl. When the solution is cooled pure carnallite separates. Variations of this method use solutions containing different ratios of MgCl_2 to KCl. In another method, the MgCl_2 is dissolved out of the carnallite with cold water, leaving the KCl behind.

14. Separation of dissolved substances in the same solution. Societe Industrielle et Commerciale de la Compagnie des Salins du Mudi, Fr. 1,075,071, October 12, 1954. CA 53 11490d.

A process is described whereby sylvinite containing 30% KCl , 55% NaCl , 10% insolvent, 3% CaSO_4 , 2% water, CaCl_2 , and MgCl_2 is placed in a tank with $110^\circ \text{H}_2\text{O}$, flowing counter-current to raw sylvinite. The insoluble sludge remains while the dissolved salts flow to a decantation tank where it deposits the insolvent impurities not in the sludge tank. It is then cooled to 8° after a period of controlled evaporation in vacua. The resulting brine crystals are then dropped out of the tank and drained dry after pumping the supernatant liquid, under a minus vapor pressure, back to the condenser where it recovers its vapor pressure and then is returned to the dissolving vat to be resaturated, with brine. The crystals obtained are mostly KCl with a few percent NaCl .

15. Potassium Chloride. Takenobu Shibata and Haruyuki Watanabe (to Shionogi Drug Manufacturing Co.) Japan 7372, November 26, 1951 KCl recovered by treatment with mother liquor and carnallite. Ca 47 61011.
16. Potassium Chloride from carnallite. Anton Orens (to Kali Forschungs - Anstalt Gm C H) Ger. 692, 896 CA 35 4557⁴, June 6, 1940. The hot solution of carnallite is evaporated without cooling. The remaining liquor is pumped to the usual crystallizers. In this way heat is saved and the KCl is in no way inferior to that made by the old method.
17. Treatment of carnallite, Kali Forschungs - Anstalt, Gm C H (Oskar F. Kaselitz and Anton Arens, inventors) Ger. 676,406, June 3, 1939. CA 33 6536⁷. Improvement in separating KCl by gradually raising temperature to above 115° without cooling where mother liquor contains low amounts of alkali chlorides and Mg_2SO_4 .
18. Decomposition of carnallite. Deutsche Solvay-Werke A.G. (Max Mitreiter inventor) Ger. 662, 090, July 13, 1938, CA 32 7688⁸. Crude carnallite treated counterflow in the cold with saturated NaCl containing 175 g./l. Mg_2Cl_2 this yielding a suspension of impure KCl in a solution containing 300 g./l. Mg_2Cl_2 . Suspension treated to wet-classification process, thickened, diluted water and(or) KCl solution. Pure KCl is filtered off.
19. Comparative flotation of carnallite and sylvite with various amines. L. I. Stremovskii (State Inst. Mined Chem. Raw Materials, Lynbertsy Moscow Region) Gornyi Zhur (1959) NO2 72-5 CA 53 10676f.

For carnallites the best collectors were primary amines of fatty acids with 18C atoms. Clay increased collector requirements. Sylvite collected by technical amines of synthetic fatty acids and tall oil acid.

20. The flotation of KCl from the salt from Kłodawa (Poland) Maria Klimek, Edward Buntner, and Stanisława Nowak (Inst. Chem. Nieorganicznej, Gliwice, Poland). *Przemysł Chem.* 37 641-5 (1958) (English Summary) CA 53 16484d.

High concentrate of KCl can be obtained from carnallite-kieserites (Kłodawa salt) by decomposition of carnallite in cold and the flotation of KCl from the suspension. Higher aliphatic amines used as collectors. Optimum amount of collector was 30-40 g./ton and optimum flotation time 2-3 min. pH and density of suspension do not effect purity and recovery of KCl. Concentrates contained 76-80% KCl. Loss of KCl 3-5%.

21. Flotation of carnallite salts, Verkaufsgemeinschaft Deutscher Kaliwerke G.m.C.H. (Rudolph Bachmann, inventor) Ger. 931,702, August 16, 1955. CA 52 17642h. A mixture of saturated aliphatic amines (I) of 14-25 C atoms with unsaturated I of 6-16 C atoms is used as a flotation agent. Raw salt is ground and decomposed with water before flotation. Starch and (or) cellulose derivs. As well as foaming agents and (or) oils may be added before or during the flotation to increase the yield of KCl.

22. Potassium Chloride by flotation from carnallite decomposition brine, Kalivertriebsstelle G.m.C.H. Abteilung Kaliforschungsstelle (Rudolph Bachmann, inventor) Ger. 880,431, June 22, 1953. Rather pure KCl is obtained by the process. Sylvanite flotation agents may be used. CA 52 9538h.

23. Processing of carnallite containing kieserite from Kłodawa deposits. Stanisław Sikora Chemik (Gliwice) 11 -- 213-15 (1958) Process described. CA 52 20932g.

Improvement of the preparation of KCl from sea water - improved extraction of carnallite. Kirokazu Otake, Takenobu Shibata, and Hiromitsu Myojo (Shionogi Research Lab, Osaka) Ann. Repts. Shinogi Research Lab No. 2 116-20 (1952) CA 51 9103h. By concentrating at 125° and cooling KCl was extracted about 70% from bittern as carnallite, which was easily decomposed, to crystal KCl and aq. MgCl₂. KCl was almost free of NaCl.

24. Dehydration of salts. Salzdelfurth A.G. (Otto Walther, inventor) Ger. 941, 367, April 12, 1956, CA 52 20936i. Application for dehydration $MgSO_4$, $MgCl_2$, or carnallite using inductor heating.
25. Concentration of brines and deposition of salts from sea water under frigid conditions. Thomas G. Thompson and Kurt H. Nelson (Univ. of Washington, Seattle) Am. J. Sci 254 227-38 (1956). Evidence indicates some salt deposits originated from frigid conditions rather than evaporation. CA 50 9799h.
26. The results of experiments on subterranean leaching of carnallite A.E. Khod'kov, CA 53 5602h. Traudy Vsesoyuz Nauch-Issledovatel Inst. Galurgii 1953 NO28, 34-49 Referat. Zhur., Khim 1956 Abst. No. 19739. Excerpts on subterranean carnallite conducted using concentric tubes; water outside and solution inside. Depth 186 m. mean salt concentration 280 g./l.
27. Electrolysis of Aqueous solutions of mixtures of KCl and NaCl, Ferri Casciani and Edward J. Lang (to Niagra Alkali Co.) U.S. 2,715,608, August 16, 1955. Process described for separation of KCl from NaCl-KCl mixtures. Natural brines can be used such as carnallite, soly, curves of NaCl-KCl-H₂O given at 40, 60 and 80°. CA 50 707a.
28. Treatment of liquors to recover K and Mg values. Wm. B. Dancy and Robert A. MacDonald (to Int. Minerals and Chemical Corp.) U.S. 2,687,339, August 24, 1954.

Liquors containing chlorides and (or) sulfates of Mg and K are mixed with a slurry, the solid phase of which is carnallite ($KCl \cdot MgCl_2 \cdot 6 H_2O$) and the aq. phase of which is saturated with respect to $MgCl_2$. Kainite ($KCl \cdot MgSO_4 \cdot 3 H_2O$) is formed and separated from the $MgCl_2$ solution, which is evaporated to a point near saturation with respect to leischofite ($MgCl_2$ content 36-40%) NaCl and Kieserite, in addition to carnallite, crystallize from the solution which then goes to a thickener. The underflow from the thickener, containing the solid phase salts, is recycled to the initial step of the process in which kainite is formed. The overflow from the thickener, concentrated $MgCl_2$ solution, is processed to yield Mg chemicals as desired.
29. Manfred Tittle (Akad Wiss Arbeitsstelle Mineralsalzforschung, Berlin Aldershof). Ibid 457-63. The heat required for the dehydration of carnallite is 146.8 KCal per mole at 140° Q413K = 94.5 plus 10.5 plus 41.8 = 146.8 KCal.

Spraying of magnesium chloride brine to obtain magnesium chloride dehydrate in a spray drier. Manfred Schubert (Zentrale Forschungsstelle Kahlind, Sonderhausen Ger.) Ibid 464-70. Discussion of technology of the process.

30. Treatment of liquors to recover K and Mg values. Wm. B. Dancy and Robt. A. MacDonald (to International Minerals and Chemical Corp.) U.S. 2,687,339 August 24, 1954. CA 49 4953d. Process described for concentrate K and Mg salts.
31. Reactions between solid oceanic salts. Robt. Kuhn Heidelberg Beitr. Mineral u. Petrog. 3 148-68, 334 (1952) CA 47 8592i. Discuss KCl (sylvite) (I) plus $MgCl_2 \cdot 6 H_2O$ (Bischofite) (II) $KCl \cdot MgCl_2 \cdot 6 H_2O$ (carnallite) where carnallite is stable from -21 to 152.5°. Many other salts discussed.
32. Dehydration of fused carnallite Ya E. Vilynyanski and N.P. Golulechenko J. Applied Chem. (USSR) 14 39-45 (in German, 45) (1941). CA 35 8221^g. Values of equil const. were determined also composition of vapor from boiling carnallite containing various amounts of $MgCl_2$, KCl, and NaCl.
33. Dehydrating carnallite. Kali-Forschungs Anstalt G.m.C.H. (Jean d'Ans and Franz Busch, inventors) Ger. 637,061, October 20, 1936. CA 31 822^g. Two stage process described. First stage done at 120° and water vapor removed as fast as possible. This yields $KCl \cdot MgCl_2 \cdot 2 H_2O$. This is then dehydrated further.
34. The first results of the department of dehydration of carnallite N. Ya Orober Kalu (USSR) 1936, No. 618-19. Gases introduced at 500-200° and were 180-210° outgoing. Product contained 1-5% H_2O and 1-2.5% MgO.
35. Work of the All Union Institute for Halurgie on the utilization of potassium salts V.V. Vyazovov, Ibid 376-88. Includes institute studies on sylvanite, carnallite, and other raw materials.

The non-aqueous flotation and dry separation of salts E. Bischoff and K.L. Wolf (Lab. Grenzflächen, Kirchheim Bolanden, Pfalz, Ger.) Ibid 389-404. Summary of excerpts on the sedimentation or flotation of sylvite, halite, schonite, kieserite, and langbeinite from suspension in various org. liquids with a variety of flotation agents.

Rotary vacuum filters in the potash industry. Hermann Reuther. Ibid 427-47. Description with 26 illustrations of several types of industrial filters.

Magnesium chloride splitting Franz Busch, Ibid 448-56. A discussion of possible processes from corn. recovery of Mg compounds from the residual solutions after potash has been extracted from carnallite.

Thermodynamic calculations on the step wise dehydration of carnallite.

36. A new graphic representation of quinary reciprocal salt systems Kayemierz Kaniok (Inst. Technol., Wroclaw, Poland) 50 6169g. A method of representation of quinary reciprocal salt systems on a plane is described and applied to the system $\text{NaCl-KCl-MgCl}_2\text{-MgSO}_4\text{-H}_2\text{O}$.
37. d'Ans J. Der Losungsgleichgewichte (equilibrium) der Systeme der Salze ozeanischer Salzablagerungen (salt deposits) Kali-Forschungs Anstalt G.m.C.H. Berlin. Verlagsges. fur Ackerbau m.b.H 254 pp. CA 27 4159.
38. Use of four dimensional geometry for construction of equilibrium and physico-chemical diagrams V.P. Radishev (Russian ---) CA 44 9227b. A polythermal course of the carnallite triple point in the quaternary system $\text{H}_2\text{O-NaCl-KCl-MgCl}_2$ is given in four coordinates. Also cryst of sea water according to Van't Hoff.
39. Kinetic determination of soly. equilibria in the sylvite and carnallite sodium chloride field of the quinary system at 20° and presentation in multicomponent diagrams VII. H. Tollert and G. Burns (Salydetfurth A.G., Empelde, Hanover, Ger.) Chem. Ing. Tech. 28 481-6 (1956) CA 50 14319i. Detailed reports are presented where equilibrium components of two salts are plotted against a fixed concentration of two other salts. They are called "Raster" diagrams.
40. Kinetic and stationary determination of solution equilibriums of easily soluble salts and their thermodynamic principles for the explanation of the metastable state of saturation by aid of the hydration enthalpies, Hans Tollert, Z physik chem. (Frankfurt (N.F.)) 6 242-60 (1956) CA 50 6169e. Differences appearing in the saturation concentrations of the quaternary system $\text{H}_2\text{O-NaCl-KCl-MgCl}_2$ as

detailed by the Van't Hoff stationary and the Farsten kinetic methods (cf. CA 49 7343c). Were studied theoretically and led to a hydrate theory of easily sol. salts and the systems of higher order thereof. The metastable state of saturation of solutions of easily sol electrolytes is interpreted as a form of oversaturation hysteresis characterized by a higher thermodynamic potential. The calculations interpreting the effects quantitatively are given in detail. The practical importance of the new theory for controlling technical solution and crystallization processes of salt systems as used in the alkali industry is pointed out.

41. Kinetic determination of solution equilibrium O Karsten (Ver. Kaliwerke Salzdelfurth, A.G., Empelde, Hannover, Ger.) Z Anorg. u allgem. Chem. 276 267-74(1954) CA 497333g.

A Solution is in equilibrium with solids when the rate of solution of the solid phases is zero. The linear relation between the concentration of a dissolved substance and its rate of solution permits determination of the equil concentration C_S of the dissolved substance. For a binary system of the equation is $C_S = C_A + \frac{V_A(C_A - C_1)}{V_1 - V_A}$

Where C_A and C_1 are concentrations less than, but nearly equal to C_S and V_A and V_1 are the associated rates of solution which can be detailed by experiment. Similar equations are determined for ternary and higher systems, and the C_S values calculated for the system NaCl - KCl - $MgCl_2$ - H_2O at 20° are Na_2Cl_2 4.06 moles, $K_2Cl_{24.97}$ moles, and $MgCl_2$ 69.41 moles. The data also provide information concerning metastable solutions in this system.

42. Preparation of KCl from Carnallite I: Graphical computation for the hydrolysis of carnallite by means of the five components diagram for oceanic salts Shumpei Oka and Minoru Kadota (Tokyo University) J. Chem. Soc. Japan Ind. Chem. Sect. 56 337-9 (1953), CA 48 11013c. Isothermal phase diagrams of three components (KCl-Mg Cl_2 - H_2O) as well as five components (NaCl KCl-Mg Cl_2 $MgCl_2$ Mg_2SO_4 Na_2SO_4) were constructed. The amount of H_2O to all to carnallite (I) for hydrolysis was calculated to be 86.3%.
43. Preparation of KCl from carnallite II: Experimental verification on the validity of the graphical computation for the hydrolysis of carnallite by means of the five component diagram for oceanic salts. Ibid 56 393-4 (1953), CA 48 11737h. Good agreement was found with the theoretical results.

44. Preparation of KCl from Carnallite III. Discussion - Ibid 56 471-3 (1953) Results of Nishimuri (CA 11 2719) were checked. Validity of the method was confirmed. CA 48 13176h.
45. Preparation of KCl from Carnallite IV. Graphical computation of hydrolysis at various temperatures and the limit for the carnallite (I) composition for the application of the hydrolysis method. Ibid 56 564-6, CA 13176i. Limit of the hydrolysis method was found to be 0.8 of the KCl/Mg 2 SO₄ ratio of I at 25°.
46. K salt production from Austrian waste brines Berg. u huttenmann. Monatsh monton. Hachschule Leoben 93 15-17 (1948), CA 42 8425i. K precipitated as carnallite. Solv curve of KCl and NaCl in MgCl₂ solution is given.
47. Use of four dimensional geometry for construction of equilibrium and physicochemical diagrams V.P. Radischev I. Zvest. Sektara Fiz-Khim Anal Inst. Obschchei i Neorg. Khim, Akad. Nauk S.S.S.R. 15 5-35 (1947) CA 44 9227b. The use of four dimensional coordinates is explained and illustrated on:
 - (a) Pb-Sn-Sn-Bi
 - (b) Polythermal course of the carnallite triple point in the system H₂O-NaCl-KCl-MgCl₂.
 - (c) Polytherm of the reciprocal system NaK 11 F, Cl, Br.
 - (d) 25° isotherm of the crystallization of sea water according to Van Hoff.
 - (e) Natural crystallization of sea water.
48. Investigation of metastable solubilities in systems of salts of oceanic salt deposits. J. d'Ans Kali 38 42-9 (1944) Chem. Zentr. 1944 II 402. CA 40 6328².
49. Solubilities in the system KCl - MgCl₂ H₂O and NaCl - MgCl₂ - H₂O at temperatures up to 200°C. J. d'Ans and G. Sipiena Kali 36 89-95 (1942), CA 34 4960². Two types of conversions have been used to obtain KCl from carnallite. Complete discussion of these is given.

50. Equilibria in the saturated solutions of salts occurring in sea water, II. Quarternary system. Iver Igulerud and T.G. Thompson, J. Am. Chem. Soc. 58 2003-9 (1936). The isotherm for the system MgCl_2 , CaCl_2 -KCl- H_2O was detailed at 0° . Solid phases were KCl, $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$ and KCl $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$. The isotherm shows the extreme insol. of KCl and carnallite in MgCl_2 solutions. Ca 31 1687⁶.
51. Solubility of the carnallite system N.S. Kurnakov, D.P. Manvev and N.A. Osokoreva. Kali NO. 2 25 (1032) Soly tables for: KCl-NaCl- MgCl_2 - H_2O at 25° and 100° plus KCl-NaCl- H_2O , NaCl- MgCl_2 - H_2O , KCl- MgCl_2 - H_2O , curves for these systems for 10 - 110° and soly curves for KCl- H_2O , NaCl- H_2O , $\text{MgCl}_2 \cdot \text{H}_2\text{O}$ for 10 - 110° .
52. Aqueous solutions at high temperatures II, E.I. Akhumov and B.B. Vasilev, J. Gen. Chem (USSR) 2 282-9 (1932), Cf CA 26 1500 27 219. CA 27 2371³. Equil drag for KCl, NaCl, MgCl_2 , H_2O given at 125° , 150° , 200° and 265° .
53. Equilibria of the solutions in the system NaCl-KCl- MgCl_2 - H_2O N.A. Osokoreva, M.A. Opuikhtena, D.N. Shoiket, E.F. Plaksina, Trans. Inst. State Applied Chem. (USSR) 1932 NO 16, 24-47 (cf Kurnakov and Zhemchuzhnyi CA 17 3271) CA 29 308⁸.

The isotherms and polytherms of NaCl-KCl- $\text{MgCl}_2 \cdot \text{H}_2\text{O}$, NaCl- MgCl_2 , KCl, $\text{MgCl}_2 \cdot \text{H}_2\text{O}$ were plotted at 10 , 20 , 25 , 40 , 50 , 60 , 70 , 100 and 110° and results tabulated. The curves obtained for the system supplement van't Hoffs data. The determination of KCl and NaCl in the final stages of crystallization led to values different than van't Hoff, and K & Z. (see above). A mean curve obtained for the mutual soly of NaCl and KCl in the presence of MgCl_2 has practical application in reworking of Solikamsk sylvites and carnallites. (see CA 26 1500 - 28 5607).
54. Garrett, D.E., Chem. Engr. Prog. 59, No.10, '59-64 (October, 1963) Crystallization of Potash. Processing of the more complex deposits of potash ores or brines.
55. Hadzeriga, Pablo. "Some Aspects of the Physical Chemistry of Potash Recovery by Solar Evaporation of Brines". Paper presented at the Rocky Mountain Minerals Conference, Soc. of Mining Engineers of A.I.M.E., Salt Lake City, Utah, Sept. 1963.